previously which has an infinite number of changes in slope; i.e.,

$$\frac{(C_L/C_D)_{\text{flap}}}{(C_L/C_D)_{\text{plate}}} - 1 = \epsilon \left(\frac{2\gamma}{\gamma - 1}\right)^{1/2} \frac{|\lambda_\infty|}{1 + |\lambda_\infty|} \qquad (12)$$

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High-Temperature Kinetics of Graphite Oxidation by Dissociated Oxygen

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Introduction

THE need to predict graphite and charring plastic ablation heat-shield behavior for atmospheric entry vehicles has motivated a great deal of recent research on the oxidation rate of graphite.[1–8] Based on this work a generally accepted overall picture has emerged (cf., Fig. 1) in which one distinguishes three fundamentally different regimes: 1) chemically controlled heterogeneous oxidation, 2) diffusion controlled heterogeneous oxidation, and 3) a sublimation regime in which the carbon oxidation reactions are "forced off" the surface. Among the assumptions that have been used to analyze the position and structure of the transition from chemically controlled to diffusion controlled heterogeneous oxidation two seem particularly suspect, namely, 1) the assumption that the specific reactivity of graphite has a simple Arrhenius behavior, and 2) the assumption that oxygen atoms play no role in the kinetics of graphite oxidation. As will be seen, these assumptions are not justifiable, and the effects of relaxing them are especially large for the case of lifting re-entry from earth orbit.

This situation can be anticipated on the following grounds. Several calculations (e.g., those of Ref. 7) based on the preceding assumptions reveal that a substantial portion of the re-entry trajectory of such vehicles takes place in this so-called "intermediate" kinetic-diffusion regime. Early entry into the diffusion-controlled regime is predicted[7] only using an unrealistic upper limit for the reactivity of commercial graphite in O_2 environments, a fact that can be verified by noting that the oxidation probability§ ϵ, corresponding to these "fast" kinetics, exceeds unity at surface temperatures above ~1200°K. In reality, of course, ϵ cannot exceed a number of order unity, and hence, simple Arrhenius behavior does not extend to these temperatures.¶ The assumption that O atoms, if present, should play no role in the kinetics[8] runs counter to existing experimental data for this[9] and similar[10–14] surface reactions. Actually, for radiation-cooled lifting re-entry vehicles, one expects nonequilibrium concentrations of O atoms at the gas/solid interface, since oxygen atom recombination in the boundary layer is negligible owing both to the low-density levels and high surface temperatures.[15–17] For these reasons, we have initiated studies of the true kinetics of the high-temperature oxidation of graphite and related refractory materials by oxygen atoms and oxygen molecules in the same apparatus. Some preliminary experimental results for graphite and their implications for ablation analyses are discussed below.

Experimental

The techniques used to study the true kinetics of graphite attack by both O atoms and O_2 are similar to those used in our previous studies of the molybdenum and tungsten reactions.[11–13] Briefly, our apparatus consists of a part Vycor-part Pyrex vacuum flow system coupled to a 25 liter/sec mechanical pump. Metered argon/O_2 mixtures are passed through a 2450 Mc/sec, 125-w microwave discharge cavity, downstream of which the gas encounters an electrically heated graphite filament fed by a regulated dc power supply. Simultaneous with a current measurement, the voltage drop across the central 0.55 cm of the filament is monitored using spring loaded contacts leading to a recording potentiometer. During an experiment the filament is maintained at constant temperature by altering the current in accord with an optical pyrometer output, thereby allowing the decrease in filament diameter caused by the reaction to be related to the increase in electrical resistance. The absolute value of the surface temperature is determined from the pyrometer reading, as corrected using the emittance-temperature relation for the specimen.[18] O atom concentrations in the vicinity of the filament are obtained using the NO_2 light titration technique.[19] The data reported here were obtained using commercially available 20-mil-diam graphite rods.** In all cases, external diffusion as well as thermal accommodation limitations were ruled out on the basis of the absence of flow rate and carrier gas effects on the observed reaction rates. This invariance of the observed reaction rates under changes in aerodynamic parameters is not unexpected under the present experimental conditions, which corresponded to a Knudsen number of about $\frac{1}{10}$, a Reynolds number of about 10 (both based on gas properties of the approach flow, using filament diameter as the reference length), and Mach numbers up to 0.6.

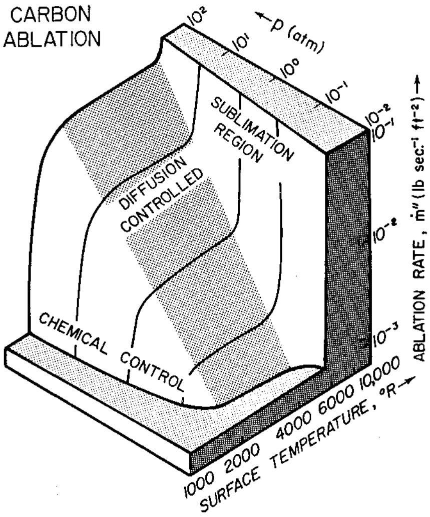

Fig. 1 Stagnation point ablation regimes for graphite in air (constructed from calculations reported in Refs. 2 and 6; nose radius = 1 ft).

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§ This is defined, for example, as the fraction of O_2 collisions with the surface that lead to carbon atom removal from the lattice.

¶ Interestingly enough, if one fits all available lower temperature ($T_w < 1200$°K) $C(s) + O_2(g)$ data by the locally Arrhenius form $\epsilon = \epsilon_0 \exp(-E/RT)$, one finds that the pre-exponential factor ϵ_0 exceeds unity. Thus, simple high-temperature extrapolations of such data are inaccurate for the same reason.

** Electrographitic extruded rod, Grade 580, No. 710 V manufactured by the Speer Carbon Co., Pa.

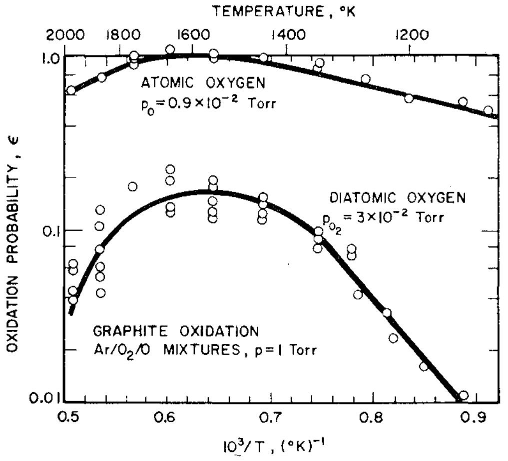

Fig. 2 Oxidation probabilities for the attack of graphite by atomic and diatomic oxygen.

Results and Discussion

Figure 2 shows our preliminary results for the temperature dependence of the oxidation probability ϵ, defined here as the ratio of the flux of carbon atoms (regardless of their chemical state of aggregation) away from the surface to the collision flux of O or O_2 with the surface. The following features are noteworthy. 1) O atom strikes are significantly more effective than O_2 in removing carbon atoms from the lattice. The O atom reaction appears to occur with essentially unit probability over a temperature interval of more than 100°K. 2) Neither reaction probability displays simple Arrhenius behavior, and each exhibits a maximum in the temperature interval shown. For the O_2 case similar maxima have been observed in the past.[20] 3) In addition, whereas the oxidation by O_2 exhibited complex departures from simple power law kinetics, we have found the O atom reaction to be first order (i.e., ϵ is independent of oxygen atom partial pressure). 4) Our data below 1400°K (which includes an experiment at 380°K) confirm the low activation energy ($\sim$6.8 Kcal/mole) of the O atom attack mechanism. These data, as well as the estimate of Ref. 21, suggest that the rate of the low-temperature $C(s) + O$-atom reaction cited in Ref. 9 is low by more than one order of magnitude. Since an incident O atom either recombines, reflects, or leads to oxidation, it is also evident that oxidation becomes the favored reaction path as the graphite surface temperature increases. 5) The removal of a carbon atom due to an O atom strike is evidently more than 300 times more probable than in the case of an N atom strike (leading to the ultimate formation of C_2N_2)[22] over the temperature range shown.

Aside from their bearing on lifting re-entry heat-shield response and simulation requirements[16] these preliminary results have implications for ballistic re-entry vehicles, especially in connection with high-altitude detection. They also suggest that the experimental techniques discussed previously are capable of providing precise kinetic data on the attack of refractory and other heat-shield materials by free radicals over a wide range of reactant concentrations and surface temperatures. These data, which are not complicated by the effects of fluid dynamic and transport parameters,[23,24] are necessary to form the basis of more realistic ablation predictions.

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